

formational analysis of the triphenylphosphine molecule in the free and solid states. Our finding, that the azimuth of the phenyl group about the P–C(phenyl) bond is arbitrary, confirms the earlier observations of Horrocks & Greenberg (1971).

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## 6-*exo*-Hydroxy-2-*exo*-methylbicyclo[2.2.1]heptane-2,6-carbolactone

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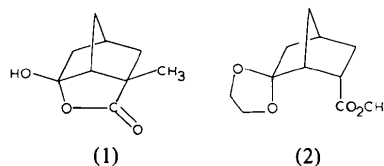
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**Abstract.** C<sub>9</sub>H<sub>12</sub>O<sub>3</sub>,  $M_r = 168.18$ , orthorhombic, *Pbca*,  $a = 16.361(3)$ ,  $b = 10.390(3)$ ,  $c = 9.757(4)$  Å,  $U = 1658.6$  Å<sup>3</sup>,  $Z = 8$ ,  $D_x = 1.35$  Mg m<sup>-3</sup>,  $\mu(\text{Mo } K\alpha) = 0.71$  mm<sup>-1</sup>.  $R = 0.031$ ,  $R_w = 0.035$  for 1094 unique diffractometer data. The title compound exists as the closed hydroxy-lactone form in the solid, with appreciable distortions from the idealized geometry.

**Introduction.** The title compound (1) (m.p. 401–402 K) was prepared by methylation of the ester acetal (2) followed by hydrolysis of the acetal and ester groups (Whittleton, 1980).



Intensities of 1806 reflexions ( $2\theta \leq 54^\circ$ ) were measured for a crystal of edges  $0.4 \times 0.3 \times 0.3$  mm, grown by slow evaporation of a solution in ethyl acetate–cyclohexane, with an Enraf–Nonius CAD-4 diffractometer and graphite-monochromatized Mo  $K\alpha$  radiation. Equivalent reflexions were merged to give

1094 reflexions having  $I \geq 3\sigma(I)$  which were employed for structure determination and refinement. Cell dimensions were obtained by least-squares refinement of 12 strong reflexions. The structure was solved by direct methods (Sheldrick, 1976), and refined by full-matrix least squares (Stewart, Kruger, Ammon, Dickinson & Hall, 1972) with weights derived from counting statistics and the scheme of Dunitz & Seiler (1973). At an intermediate stage, the positions of all H atoms were

located from a difference map and subsequently refined with isotropic temperature factors; all other atoms were refined with anisotropic thermal parameters. An extinction correction was applied in the final stages. Positional and mean thermal parameters are given in Table 1.\* The molecular and crystal structures are depicted in Figs. 1 and 2 and the atomic numbering

Table 1. Atomic coordinates and isotropic  $U$  values ( $\times 10^4$ ; *e.s.d.*'s in parentheses)

Non-hydrogen atoms were refined anisotropically;  $U_{eq} = \frac{1}{3}(U_{11} + U_{22} + U_{33})$ .

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{eq}/U$ ( $\text{\AA}^2$ )
C(1)	911 (1)	4813 (2)	3841 (2)	304 (8)
C(2)	627 (1)	4807 (2)	2333 (2)	300 (8)
C(3)	1071 (1)	6036 (2)	1754 (2)	382 (10)
C(4)	1613 (1)	6463 (2)	2943 (2)	416 (10)
C(5)	2282 (1)	5456 (2)	3187 (2)	427 (10)
C(6)	1780 (1)	4286 (2)	3661 (2)	333 (9)
C(7)	1060 (1)	6233 (2)	4176 (2)	411 (10)
C(8)	1051 (1)	3638 (2)	1761 (2)	356 (9)
C(9)	-292 (1)	4809 (2)	2093 (2)	439 (11)
O(1)	874 (1)	3016 (1)	760 (1)	532 (8)
O(2)	1708 (1)	3351 (1)	2515 (1)	407 (7)
O(3)	2128 (1)	3663 (1)	4753 (1)	460 (7)
H(1)	583 (11)	4295 (18)	4469 (19)	358 (47)
H(31)	651 (12)	6675 (18)	1535 (19)	399 (50)
H(32)	1368 (12)	5843 (17)	926 (21)	386 (50)
H(4)	1819 (12)	7305 (21)	2820 (20)	456 (54)
H(51)	2596 (15)	5238 (21)	2374 (26)	574 (62)
H(52)	2628 (13)	5729 (22)	3925 (23)	556 (62)
H(71)	1341 (13)	6348 (18)	5042 (22)	454 (52)
H(72)	545 (13)	6747 (20)	4158 (19)	470 (55)
H(91)	-554 (14)	5582 (23)	2517 (24)	641 (68)
H(92)	-548 (14)	4017 (25)	2472 (24)	651 (66)
H(93)	-401 (17)	4822 (25)	1120 (29)	782 (77)
H(OH)	1762 (17)	3108 (27)	5051 (30)	810 (89)

$U_{eq}/U$   
( $\text{\AA}^2$ )

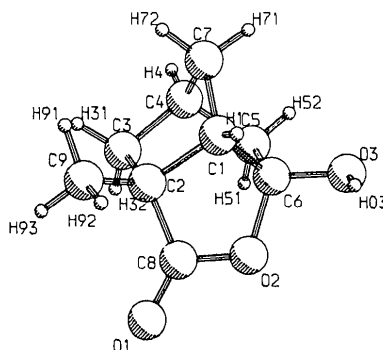


Fig. 1. View of (1) drawn by program *PLUTO 78* (W. D. S. Motherwell, Univ. of Cambridge).

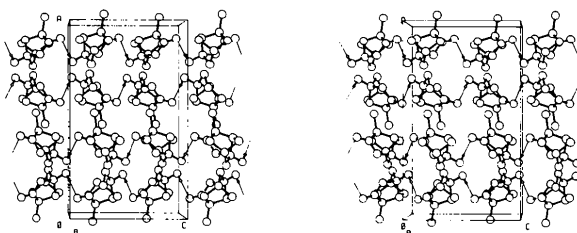


Fig. 2. Stereoscopic view of the crystal structure of (1) (drawn by *PLUTO 78*).

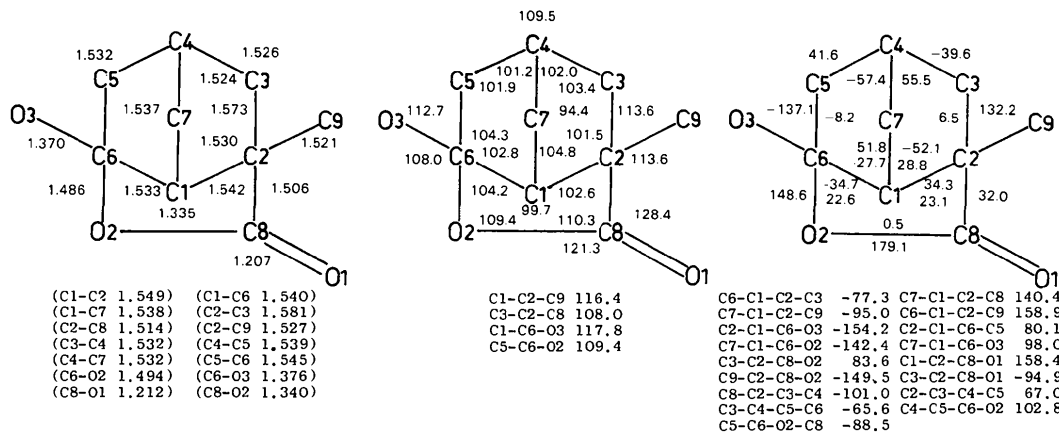
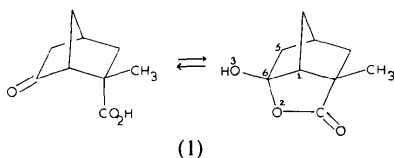


Fig. 3. Bond lengths ( $\text{\AA}$ ) (values corrected for molecular libration in parentheses), bond angles ( $^\circ$ ) and torsion angles ( $^\circ$ ). Estimated standard deviations are *ca* 0.0025  $\text{\AA}$  for bond lengths, 0.15 $^\circ$  for bond angles and 0.2 $^\circ$  for torsion angles, not involving H atoms. The ranges of bond lengths and angles involving H are C-H 0.94-1.00, O-H 0.88  $\text{\AA}$ , H-C-C 108-119, H-C-H 107-112, H-O-C 106 $^\circ$ .

system, bond lengths, angles and torsion angles in Fig. 3.

**Discussion.** The title compound (1) may in principle exist as either an 'open' keto-acid or a 'closed' hydroxy-lactone.

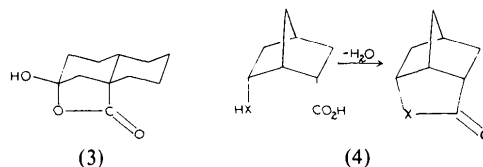


Solid-state infrared studies (Whittleton, 1980) indicate a preference for the closed form which is confirmed by this X-ray structure determination.

Molecules such as (1) are of interest to us since they can provide information about the reaction pathway separating a  $\gamma$ -keto-acid and the corresponding hydroxy-lactone. In this connexion, the geometry at the geminally dioxo-substituted carbon, C(6), is especially noteworthy. The O(3)—C(6) bond is short (1.37 Å) compared with the usual bond length of 1.43 Å in alcohols, whereas the endocyclic O(2)—C(6) bond is long (1.49 compared with 1.47 Å for normal lactones). These 'antisymmetric stretching' distortions are accompanied by corresponding bond-angle distortions: the CCO angles involving exocyclic O(3) [C(1)—C(6)—O(3) 117.8, C(5)—C(6)—O(3) 112.7°] are considerably larger than the comparable angles involving endocyclic O(2) [C(1)—C(6)—O(2) 104.2, C(5)—C(6)—O(2) 109.4°]. The stretching and bending at dioxo-substituted carbon has been shown to correlate according to the equation  $173\Delta d = \Delta\beta$ , where  $\Delta d$  is the difference in length of the two C—O bonds and  $\Delta\beta$  is the difference in the sums of the CCO angles for the two oxygen substituents (Bürgi, Dunitz & Shefter, 1974); in this case,  $\Delta d$  (1.486 — 1.370) = 0.12 Å and  $\Delta\beta$  (117.8 + 112.7 — 104.2 — 109.4) = 16.9°, in reasonable agreement with previous results.

The pattern and magnitude of distortions observed here closely follow those found in a previous study of the analogous decalin hydroxy-lactone (3) (Chadwick & Dunitz, 1979) ( $\Delta d$  = 0.128 Å,  $\Delta\beta$  = 19.5°). The hypothetical, undistorted molecules must be of higher energy and the relaxation to the observed geometries be accompanied by a lowering of the strain energy of the tricyclic ring systems. This strain energy is not expected to be large: NMR studies on (3) (Chadwick & Dunitz, 1979) and on the demethyl analogue of (1) (Whittleton, 1980) show that the energy barriers separating open and closed forms (*ca* 30 kJ mol<sup>-1</sup>) and the free-energy ( $\Delta G^\circ$ ) differences between these forms [*ca* 5 kJ mol<sup>-1</sup> for demethyl-(1) and 10 kJ mol<sup>-1</sup> for (3)] are low. In addition, molecular-mechanics calculations (Allinger & Sprague, 1972) suggest that little extra strain is introduced into the norbornane system by closure of the type shown in (4). The evidence

therefore points to a rather flat energy profile along the reaction coordinate for ring opening (and closure): this combined with the occurrence of similar distortions in (1) and (3) encourages us to view these distortions as an expression of movement along this reaction path, *i.e.* of incipient breakdown of the hydroxy-lactone system to the separated nucleophilic and electrophilic centres contained in the open keto-acid. It is significant that in both (1) and (3) whereas the CCO bond angles at the dioxo-substituted carbon are considerably distorted in general, the OCO angles are close to tetrahedral [107.9 in (3), 108.0° in (1)]. Thus, as the leaving group departs and the remaining oxygen moves towards the C(1)—C(6)—C(5) plane (the ketonic plane of the keto-acid isomer) a roughly tetrahedral angle is maintained between the departing atom and the potential carbonyl group. Dunitz (1975) has pointed out that nucleophiles tend to attack ketonic carbonyl groups along a trajectory subtending a roughly tetrahedral angle at the carbonyl group. The maintenance of this preference for a tetrahedral angle in the breakdown of hydroxy-lactones (1) and (3), and its occurrence in the majority of the 24 related molecules examined previously (Bürgi, Dunitz & Shefter, 1974), may be interpreted as a nice (structural) example of the principle of microscopic reversibility.



Two further interesting structural features are common to (1) and (3). In both cases, the hydroxyl hydrogen is disposed such that a lone pair on the exocyclic oxygen (assuming *sp*<sup>3</sup> hybridization) is almost exactly antiperiplanar (*ap*) to the lengthened, endocyclic C—O bond [the relevant H—O—C—O torsion angles are -69 for (1) and -74° for (3)]; Deslongchamps (1975) has demonstrated the importance of *ap* lone pairs in the cleavage of C—O bonds during the breakdown of orthoesters and related compounds. Both (1) and (3) show similar patterns of intermolecular hydrogen bonding in which the OH hydrogen atom bonds to the carbonyl oxygen of an adjacent molecule forming chains through the crystal. If this mimics the kind of proton transfers that occur in solution, then the preferred mode of hydroxy-lactone ring opening involves protonation on the carbonyl rather than on the ring oxygen, *i.e.* the mechanism resembles, at least in the early stages, ester rather than acetal hydrolysis (Bamford & Tipper, 1972, 1977). Fife (1965) proposed the alternative pattern of protonation in a kinetics study of the mechanism of hydrolysis of  $\gamma$ -ethoxy- $\gamma$ -butyrolactone: the data presented are not definitive on this point, however.

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## Structure of *cis*-3,3-Dimethyl-2,4-dioxa-7-thiabicyclo[3.3.0]octane 7-Oxide Monohydrate

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**Abstract.** C<sub>7</sub>H<sub>12</sub>O<sub>3</sub>S.H<sub>2</sub>O, monoclinic, space group *A2/m*,  $a = 6.484(1)$ ,  $b = 8.995(3)$ ,  $c = 15.899(3)$  Å,  $\beta = 92.37(1)^\circ$ ,  $V = 926.5$  Å<sup>3</sup>,  $Z = 4$ ,  $M_r = 194$ ,  $F(000) = 416$ ,  $\mu = 29.9$  cm<sup>-1</sup>. The structure was solved by the heavy-atom method and refined by full-matrix least-squares computations to  $R = 0.064$  for 819 observed reflections. The dihedral angle between atoms H2(C1) and H(C2) (respectively in equatorial and axial positions on the S heterocycle), through the C(1)–C(2) bond, is close to 90°, as had been predicted by Lett & Marquet [*Tetrahedron Lett.* (1974). **30**, 3365–3377] from NMR measurements.

**Introduction.** This crystal structure is the last of a series of X-ray studies of some bicyclic sulfoxides (Stora & Marquet, 1973; Stora, 1974; Lefebvre & Robert, 1974) which have structural analogies with biotin (Lett & Marquet, 1974). It has been undertaken to study the respective positions of the S heterocycle H atoms which are not substituted in this new molecule.

The space group (systematic absences:  $k + l = 2n$ ) is *A2/m*. The unit-cell dimensions were refined from 35 reflections ( $\theta$  up to 54°), manually set on a CAD-3 diffractometer with Cu  $K\alpha$  radiation ( $\lambda = 1.5418$  Å), 19 of them having  $\theta$  ca  $\pm 15^\circ$ . The density was

determined by flotation in CHCl<sub>3</sub>/C<sub>6</sub>H<sub>6</sub>. The measured value, 1.40 g cm<sup>-3</sup>, was greater than that calculated, 1.261 g cm<sup>-3</sup>, before a water molecule was discovered. The calculated density was then 1.392 g cm<sup>-3</sup>, in agreement with only half a molecule in the asymmetric unit, *i.e.*  $Z = 4$  in the cell instead of 8. We concluded that the molecule itself has a mirror plane. The crystal used for data collection was 0.30 × 0.20 × 0.50 mm. 893 intensities were measured, of which 819 with  $I > 2\sigma(I)$  were considered as observed. They were collected at 295 K in the range  $3^\circ \leq 2\theta \leq 66.8^\circ$  ( $\theta/2\theta$  scan mode), at a rate of 10° min<sup>-1</sup> (scan width =  $1.1^\circ + 0.35^\circ \tan \theta$ ). Two standard reflections were monitored every 40 reflections and they remained constant within  $\pm 3\%$ .

The S-atom position was given by Harker and Patterson maps. All the non-H atoms with one exception, O(*W*), appeared in the first Fourier synthesis. Full-matrix least-squares isotropic refinement led to  $R (= \sum |F_o| - |F_c| / \sum |F_o|) = 0.28$ , which only fell to 0.24 by anisotropic refinement, suggesting one or more water molecules were present. A difference synthesis then showed a strong peak on the twofold axis; this was assigned as an O atom, O(*W*). A new isotropic refinement of all non-H atoms led to  $R = 0.19$  which fell to 0.095 by anisotropic refinements and a difference synthesis gave all the H atoms in their expected positions, except those of the water molecule.

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